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DETAILED DESCRIPTION

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[Detailed description]

[0001]

[Field of the Invention] An efficient injection-molding method is used and this invention is a polytetrafluoroethylene (PTFE). the following -- the same -- etc. -- it is related with the technique of manufacturing the sintered compact of a fluoro-resin

[0002]

[A Prior art and Object of the Invention] Conventionally, also in 380 degrees C which will be in the melting status, 1011P and since a melt viscosity is very high, it can make PTFE resin put in practical use the Plastic solid of arbitrary configurations neither with extrusion molding nor injection molding.

[0003] Therefore, when it is going to obtain the sintered compact of a certain configuration, first, preforming of the PTFE resin powder of a raw material is carried out as it is in ordinary temperature, and the preforming field is heated and sintered at 360-390 degrees C which is beyond the melting point of PTFE resin. Although a compression forming, the ram-extrusion fabricating method, the paste extrusion method that uses an extrusion assistant are used for preforming, any technique is carrying out the cutting of the sintered preforming field, in order to deal in the sintered compact of a desired configuration, since configuration degree of freedom is scarce.

[0004] Thus, since a manipulation cycle is long, a cost attaches highly a manufacture of PTFE resin sintered compact of a desired configuration. Moreover, in the case of the complicated configuration, the cutting is difficult.

[0005] These problems exist also about the fluoro-resin whose melt viscosities other than PTFE are 105-1013P.

[0006] this invention is made in view of the aforementioned trouble, and the purpose is in offering the technique of obtaining the fluoro-resin sintered compact of a desired configuration efficiently.

[0007]

[The means for solving a technical problem] That is, this invention relates to the manufacturing method of the fluoro-resin sintered compact characterized by sintering after mixing fluoro-resin powder and at least one sort of low-temperature resolvability binders, injection molding mixture and carrying out degreasing processing of the Plastic solid.

[0008]

[An operation and an example] According to the manufacturing method of this invention, injection molding can also use as a fluoro-resin sintered compact in itself the fluoro-resin whose difficult melt viscosity is 105-1013P using injection molding. The other fluoro-resin of a melt viscosity can also be used on condition that it says [ that the melting point is higher than the decomposition temperature of the binder to use ].

[0009] the ratio which measured by the following technique with the melt viscosity in this invention using the position TMA (product made from Physical science Electrical machinery) under a \*\*\*\*\* Rex sample in the case of PTFE -- in the case of fluoro-resins other than a melt viscosity and PTFE, the melt viscosity measured by the following technique using the capillary-tube flow tester (Shimadzu

Make) is meant

[0010] In the case of measuring method (1);PTFE, it is :ratio melt viscosity (the temperature of 380 degrees C, and load 0.8kg/cm<sup>2</sup>).

A creep test is performed and measured in the following procedures using "the position TMA under a \*\*\*\*\* Rex sample" (product made from Physical science Electrical machinery).

[0011] First, a sample is produced by the following technique. A piece of paper is filled up on both sides of 80g powder, a pressure is gradually put on the metal mold of a cylindrical shape with a bore of 50mm for about 30 seconds, and it is 2 the last pressure of about 352kg/cm. It is made to become and maintains at this pressure for 2 minutes. Next, a Plastic solid is taken out from metal mold, it calcinates [ for 90 minutes ] and \*\*\*\*s to 250 degrees C the speed for 1 degree-C/continuously in the air electric furnace which carried out the temperature up to 371 degrees C, and it takes out, after maintaining for 30 minutes at this temperature. In accordance with the side face, the cutting of the baking field of this cylindrical shape is carried out, and it deals in a band-like sheet with a thickness of 0.5mm.

[0012] From this sheet, a wafer with a width of face [ of 4mm - 5mm ] and a length of 15mm is cut off, width of face and thickness are measured correctly, and the cross section is calculated. Sample insertion metallic ornaments are attached in the ends of a wafer so that the distance between insertion may be set to 1.0cm. The assembly of this metal-sample is put into circular cylinder-like kiln, a temperature up is carried out even to 380 degrees C from a room temperature the speed for 20 degrees-C/, and this temperature (380 degrees C) is held. After holding for about 5 minutes, the load of about 15g is applied. From the curve of time change of elongation, the elongation for [ of an after / a load / 60 minutes - ] 120 minutes is read, and the rate over time (60 minutes) is searched for. a ratio -- a melt viscosity is calculated from the following relational expression

[0013]

[A-one number]

$$\eta = \frac{W \times L_r \times g}{3 \times (dL_r / dT) \times A_r}$$

但し、 $\eta$  = 比溶融粘度 (ポアズ)

W = 引っ張り荷重 (g)

$L_r$  = 試料の長さ (380°C) (cm)

g = 重力の定数 980cm/秒<sup>2</sup>

$dL_r / dT$  = 60分～120分の間の伸びの時間に対する割合  
(cm/秒)

$A_r$  = 試料の断面積 (380°C) (cm<sup>2</sup>)

ここで、別に求めた熱膨張の測定から、 $L_r / A_r$ は次式を用いて計算することができる。

$L_r / A_r = 0.80 \times L$  (室温での長さ)

/ A (室温での断面積)

[0014] In the case of fluororesins other than measuring method (2);PTFE, a melt viscosity is measured for each fluororesin by the following temperature and loads using :capillary-tube flow tester (Shimadzu Make).

[0015]

[Table 1]

表 1

フッ素樹脂	温度 (°C)	荷重 (kg/cm <sup>2</sup> )
P F A	380	7
F E P	380	7
P C T F E	240	100
P V D F	230	7
E T F E	300	7
E C T F E	300	7

[0016] As a fluoro resin whose melt viscosity is 105-1013P, the copolymer which consists of the homopolymers of a tetrafluoroethylene (TFE), the perfluoroalkylvinyl ether, a hexafluoro propene, a chlorotrifluoroethylene, or the vinylidene full ora id or those two sorts or more or the copolymer of TFE and ethylene, the copolymer of \*\*\*\*\* fluoro ethylene and ethylene, etc. are raised, for example.

Specifically, PTFE, a tetrafluoroethylene / perfluoroalkylvinyl ether copolymer (PFA), a tetrafluoroethylene / hexafluoro propene copolymer (FEP), a polychlorotrifluoroethylene resin (PCTFE), a polyvinylidene fluoride (PVDF), ethylene / tetrafluoroethylene copolymer (ETFE), a chlorotrifluoroethylene / ethylene copolymer (ECTFE), etc. are raised. PTFE, PFA, and FEP are raised more preferably. The ground is that the temperature gradient of the decomposition temperature of a low-temperature resolvability binder and the melting point of a fluoro resin to use is large, degreasing and sintering are performed easily, and it gets.

[0017] A melt viscosity is 105. Injection molding usually performed is more possible than the former for the fluoro resin of under a poise, and the weld after a degreasing and sintering is a little difficult for the fluoro resin exceeding 1013P.

[0018] The powder of the homopolymer of TFE and the copolymer of TFE which denaturalized by 2 or less % of the weight of the copolymerization nature monomer is contained in PTFE resin powder. As this modifier, the perfluoro alkene (for example, hexafluoropropylene) of carbon numbers 3-6, the perfluoro (alkyl vinyl ether) (for example, perfluoro (propyl vinyl ether)) of carbon numbers 3-6, etc. are raised. these denaturation copolymer -- PTFE homopolymer -- the same -- usual technique -- extrusion molding -- injection molding cannot be carried out 1000 micrometers or less of 0.01-500 micrometers of powdered mean particle diameters are 0.1-50 micrometers more preferably. When a mean particle diameter is larger than 1000 micrometers, a touch area becomes small and it is in the inclination that a mechanical strength falls.

[0019] It functions as the low-temperature resolvability binder mixed by the above-mentioned fluoro resin powder advancing an injection-molding process smoothly. that is, a fluidity gives the fluoro resin powder which a melt viscosity is high and does not flow in itself by the flowability of the binder plasticized at the time of injection molding -- having -- metal mold -- fluoro resin powder is fixed to the configuration of metal mold by the cohesive force between the molecule, when fluoro resin powder is led to the interior good and a binder carries out cooling solidification A binder is easily pyrolyzed by heating at the time of a degreasing, and although cannot leave carbide and ash content and they can be removed, a binder can also remove a binder by the pyrolysis, after performing solvent extraction to a solvent in \*\*\*\*. The mold goods after a degreasing are the porous material field.

Moreover, at the time of sintering, a fluororesin carries out melting, the whole contracts uniformly, and the high-density field of a sinter ball and a fluororesin is acquired. As for a binder, because of this uniform deflation, it is desirable that it is what can distribute fluororesin powder uniformly.

[0020] As this low-temperature resolvability binder, the organic system binder of 100-320 degrees C of decomposition temperatures is desirable. That whose decomposition temperature is 150-300 degrees C is more desirable. Here, a decomposition temperature uses thermogravimetric-measurement equipment and means the decomposition start temperature which measured the programming rate as a part for 10 degrees-C/in air. When the decomposition temperature became higher than 320 degrees C and it heats in degreasing processing for binder elimination more than a decomposition temperature, a fluororesin carries out melting, when a degreasing becomes difficult and becomes lower than 100 degrees C, a binder becomes easy to volatilize and there is an inclination for which injection molding becomes impossible. As a low-temperature resolvability binder which fulfills these conditions, a dimethyl phthalate, a diethyl phthalate, a phthalic-acid dipropyl, dibutyl phthalate, a dioctyl phthalate, stearin acid, a polymethyl methacrylate, a polymethacrylic-acid ethyl, a polymethacrylic-acid propyl, polymethacrylic-acid butyl, a polymethacrylic-acid octyl, a polyethylene glycol, a paraffine wax, a low-molecular-weight poly alpha methyl styrene, a low-molecular-weight polyoxymethylene, styrene oligomer, ethylene oligomer, propylene oligomer, etc. can be raised, for example. Stearin acid, a polymethyl methacrylate, a polymethacrylic-acid ethyl, a polymethacrylic-acid propyl, polymethacrylic-acid butyl, a polymethacrylic-acid octyl, a polyethylene glycol, a paraffine wax, a low-molecular-weight poly alpha methyl styrene, a low-molecular-weight polyoxymethylene, etc. are more preferably raised in respect of the mold-release characteristic at the time of injection molding, the ease of carrying out of a degreasing, etc. and the ease of dealing with it.

[0021] Although two or more sorts may be combined, you may use it and it is degreased by the pyrolysis, that these organic system binders are independent or after carrying out the extraction elimination of almost all the binders by the solvent, in \*\*\*\*, the remainder can also be degreased by the pyrolysis to a solvent.

[0022] If the number of binders is one, although a temperature program setup at the time of recovery of the binder by solvent extraction or a heating degreasing can be simplified, two or more kinds may be used, and a melt viscosity may use two kinds, a remarkable low binder and a high binder, so that it may explain below.

[0023] For example, a resin carries out the fibrillation of the PTFE resin powder easily by the shearing stress at the time of injection. After PTFE resin has carried out the fibrillation, when degreasing operation is performed, a Plastic solid deforms and it may stop obtaining the thing of the configuration of hope. The binder with it has the effect which suppresses the fibrillation of this PTFE among the aforementioned binders. [ a remarkable melt viscosity and ] [ low ] A paraffine wax, a polyethylene glycol, etc. are raised as a binder with it. [ a remarkable melt viscosity and ] [ low ] However, if it goes into a degreasing process, a paraffine wax has the property which a principal chain decomposes at random from per 200 degrees C, and forms a decomposition product to the low decomposition product with high molecular weight, and in case it is degreasing processing, only a low-molecular-weight decomposition product will carry out gas \*\*\*\* of it, for example. The amount decomposition product of macromolecules is also decomposed gradually after that, although reached to the molecular weight which can finally carry out gas \*\*\*\*, a long time is required, and the element of the rapid cycle molding which is the advantage of injection molding may be negated. On the other hand, powder, such as the poly alpha methyl styrene, a polymethyl methacrylate, a polymethacrylic-acid ethyl, polymethacrylic-acid butyl, a polymethacrylic-acid propyl, and a polymethacrylic-acid octyl, has the fault which the melt viscosity of a certain thing makes carry out [ effect / binder-] the fibrillation of the PTFE resin to 10P or more at 150 degrees C since it is high among the above-mentioned binders. However, since there is a property which the pyrolysis device by heating decomposes per monomer on a chain reaction target, catabolic rate can be comparatively quick and can terminate a degreasing for a short time. Therefore, it is desirable to perform degreasing processing for a short time, suppressing the fibrillation of PTFE in the case of injection by being used by blending at a suitable rate, in order to compensate the binder with it,

and the binder with the above-mentioned high melt viscosity with a mutual fault. [ the above-mentioned remarkable melt viscosity and ] [ low ] although a melt viscosity depends the remarkable blending ratio of coal of a low binder and a high binder on the modality of each binder -- 100:0-0:100 -- it is 100:1-1:100 preferably

[0024] The amount of the binder used of the above-mentioned low-temperature resolvability is more preferably set up to 20 - 40% of the weight 18 to 50% of the weight 13 to 80% of the weight in the sum on the basis of the sum weight with fluoro-resin powder. If there is less amount used than 13 % of the weight, it cannot inject smoothly, if [ than 80 % of the weight ] more, degreasing processing will take a long time, and mechanical properties, such as tensile strength of a Plastic solid, fall.

[0025] Moreover, you may add fillers, such as dispersants, such as a stearyl amine, stearin acid, polyethylene-glycol dodecylether, and perfluoro octyl ethyl stearate, and a glass fiber, a carbon fiber, to the mixture of the fluoro-resin powder which carries out injection molding, and a low-temperature resolvability binder further.

[0026] The mixture of fluoro-resin powder and a low-temperature resolvability binder is obtained by melting for example, a low-temperature resolvability binder in a solvent remaining as it is (dryblend) or suitable, and adding to fluoro-resin powder, for example, mixing by the scree one motor etc. About the fluoro-resin to which a fibrillation seldom happens, you may mix a low-temperature resolvability binder and fluoro-resin powder with kneading machines, such as a roll and a kneader. As a suitable solvent, n-hexane, methyl acetate, ethyl acetate, butyl acetate, an acetone, a methyl ethyl ketone (MEK), a methyl isobutyl ketone (MIBK), isopropyl alcohol (IPA), toluene, a xylene, etc. are raised. Furthermore, although addition mixture is carried out by usual technique when adding a dispersant, a filler, etc., a dispersant etc. can be melted in the above organic system solvents, and it can add.

[0027] For fluoro-resin powder, a low-temperature resolvability binder, and the mixture that will consist of a dispersant, a filler, etc. if it requires, the melt viscosity measured with the measuring method (2) for the lubricant effect of \*\*\*\*\* is 10-105. A poise, especially 102-104 It is desirable that it is a poise.

[0028] Although especially the technique of injection molding of the obtained mixture is not restricted, as for especially injection temperature, it is desirable to carry out in temperature of 70-200 degrees C beyond the melting point of a binder.

[0029] Next, the heating elimination of the low-temperature resolvability binder which remains in a Plastic solid by degreasing processing is carried out. Although a usual heating furnace can perform this degreasing processing, the direction is desirable although a complicated degreasing of the mold goods of a configuration is especially equipped with control functions, such as precise temperature and a pressure. Gas \*\*\*\* of the low-temperature resolvability binder is disassembled and carried out in a temperature-up phase. Since deformation by the force which an organization is going to swell or it is going to destroy will be caused in connection with gas \*\*\*\* if a programming rate is too quick at this time, as for a programming rate, it is desirable to set up in 2-35 degrees C /in an hour. If a low-temperature resolvability binder is \*\*\*\* at a solvent, the process of degreasing processing by heating can be sharply shortened by performing solvent extraction before degreasing processing by heating. The above solvents are used when dispersants, such as low-temperature resolvability binders, such as a paraffine wax and a polyethylene glycol, or a stearyl amine, stearin acid, polyethylene-glycol dodecylether, and perfluoro octyl ethyl stearate, etc. are used.

[0030] A fluoro-resin sintered compact is obtained by sintering the Plastic solid by which degreasing processing was continued and carried out. The heating temperature at the time of sintering is set as the suitable level of the fluoro-resin powder used as a raw material.

[0031] If it is before a degreasing when the molding of the sintered compact obtained according to the manufacturing method of this invention is poor, a reuse can be carried out by trituration.

[0032] Although a concrete example is next given and this invention is explained, this invention is not limited to these.

[0033] Example 1 paraffine-wax (200 degrees-C [ of decomposition temperatures ], 63 degrees C of melting points) 25g, and 4g (Daikin Industries, LTD. make) of fluorochemical surfactants It is made to melt in the mixed solvent of n-hexane 150g and IPA50g. to this 25 micrometers of mean particle

diameters, 100g (poly chlorofluorocarbon TFE M-12, melt-viscosity; 1012P:Daikin Industries, LTD. make by the measuring method (1)) of PTFE resin powder with an apparent density of 0.29g [cc] was added, and the stoving was carried out at 80 degrees C, agitating slowly by the three one motor. 9g of the powder of polymethacrylic-acid butyl (230 degrees C of decomposition temperatures, 60 degrees C of glass transition temperatures) was mixed by dryblend into this mixture, and the compound was obtained. the melt viscosity by the measuring method (2) of a compound --  $7 \times 10^3$  it was .

[0034] Injection molding of this compound was carried out using the injection molding machine (made in the Yamashiro Energy machine factory) at injection pressure 2 and the injection speed of 70mm/second of 512kg/cm, and the resin temperature (compound temperature) of 90 degrees C, and the Plastic solid was obtained. The Plastic solid was moved to the heating furnace ( elevated-temperature electric furnace FP31 type Made from \*\*\*\*\* Science) for degreasing processing, the temperature up was carried out to the next by the 10 degrees C [hour] programming rate, and the paraffine wax was removed by maintaining at 200 degrees C for 20 hours. Then, elimination of polymethacrylic-acid butyl and a fluorochemical surfactant was performed by carrying out a temperature up in 10 degrees C /in an hour, and maintaining at 250 degrees C for 5 hours. Moreover, after were not based on heating but carrying out solvent extraction of a paraffine wax and the fluorochemical surfactant using n-hexane / IPA (weight ratio = 3/1), the temperature up was carried out by the 10 degrees C [hour] programming rate, and polymethacrylic-acid butyl was removed by maintaining at 250 degrees C for 5 hours.

[0035] Next, the temperature up of the Plastic solid which carried out degreasing processing was carried out to 370 degrees C by the 70 degrees C [hour] programming rate, by maintaining to the temperature for 5 hours, PTFE resin Plastic solid was sintered, the Plastic solid was shrunk, and PTFE resin sintered compact with which the request was fabricated was obtained. The sintered compact is white and was not colored. Moreover, specific gravity was 2.10.

[0036] Combination, a measurement result, etc. of a compound are shown in Table 2.

[0037] In addition, the measurement conditions of the melt viscosity by the measuring method (2) of the compound in an example and the example of a comparison are shown below.

Melt-viscosity Equipment: Capillary-tube flow tester by Shimadzu Corp. The compound which added 20g of CFT-500C die:8mmx2.1mm load:150kg/cm<sup>2</sup> temperature:150 degree-C example 2 glass fibers was prepared, and also PTFE resin sintered compact was obtained like the example 1. Combination, a measurement result, etc. of a compound are shown in Table 2.

[0038] The melt viscosity by example 3 measuring method (2) is  $5 \times 10^6$ . PFA resin sintered compact was obtained like the example 1 by combination of a compound which is shown in Table 2 using PFA which is a poise. A measurement result is shown in Table 2.

[0039] The melt viscosity by example 4 measuring method (2) is 106. The FEP resin sintered compact was obtained like the example 1 by combination of a compound which is shown in Table 2 using FEP which is a poise. A measurement result is shown in Table 2.

[0040]

[Table 2]

表 2

項目／例	実施例 1	実施例 2	実施例 3	実施例 4
配合 (重量部)	PTFE粉末 (粒子径25 $\mu$ m)	PTFE粉末 (粒子径25 $\mu$ m)	PFA粉末 (粒子径30 $\mu$ m)	FEPP粉末 (粒子径40 $\mu$ m)
	パラフィンワックス	ガラス繊維	パラフィンワックス	パラフィンワックス
	ポリメタクリル酸 ブチル粉末	パラフィンワックス ポリメタクリル酸 ブチル粉末	ポリメタクリル酸 ブチル粉末	ポリメタクリル酸 ブチル粉末
	フッ素系界面活性剤	フッ素系界面活性剤	フッ素系界面活性剤	フッ素系界面活性剤
	合 計	合 計	合 計	合 計
配合物の 溶解粘度 (ポアズ)	100	80	100	100
射出成形	可/90℃	可/90℃	可/90℃	可/90℃
溶剤抽出	可	可	可	可
加熱脱脂	可	可	可	可
焼 結 体	なし	なし	なし	なし
比重	2.10	2.14	2.12	2.11
フッ素樹脂 粉末の溶解 粘度(ポアズ)	10 <sup>12</sup>	10 <sup>12</sup>	5 × 10 <sup>6</sup>	10 <sup>6</sup>
射出成形時 の温度(℃)	90	90	90	90

備考 溶解粘度(ポアズ)の測定法

PTFE単独のばあい:「比溶解粘度」法

配合物およびPTFE以外のフッ素樹脂のばあい:「キャピラリーフローテスト」法

[0041] PTFE resin sintered compact was obtained like the example 1 except having replaced combination of a compound with, as shown in the examples 1 and 2 of a comparison, and three tables 3. However, in the examples 2 and 3 of a comparison, it injected at the injection temperature (resin temperature) of 250 degrees C. Combination, a measurement result, etc. of a compound are shown in Table 3. In addition, the sintered compact which the melting point of the polybutylene terephthalate used

in the examples 1 and 2 of a comparison is 218-219 degrees C, and a decomposition temperature is 390 degrees C, and was obtained was colored the nigrities different from the white of a compound.

[0042]

[Table 3]

表 3

項目／例	比較例 1	比較例 2	比較例 3
配 合 (重量部)	PTFE 粉末 (粒子径 25 $\mu$ m) ポリブチレン テトラレート フッ素系界面活性剤 合 計	PTFE 粉末 (粒子径 25 $\mu$ m) ポリブチレン テトラレート フッ素系界面活性剤 合 計	PTFE 粉末 (粒子径 25 $\mu$ m) 合 計
	100 80 4 184	100 80 4 184	100 100
配合物の 溶融粘度 (ポアズ)	測定不可／150℃	$5 \times 10^4$ / 250℃	測定不可／250℃
射出成形	不可／90℃	可／250℃	不可／250℃
溶剤抽出	－	不可	－
加熱脱脂	－	不可	－
着色	－	あり	－
比重	－	1.52	－
樹脂 粉末の溶融 粘度 (ポアズ)	$10^{12}$	$10^{12}$	$10^{12}$
射出成形時の 温度 (℃)	90	250	250

備考 溶融粘度 (ポアズ) の測定法

PTFE 単独のばあい：「比溶融粘度」法

配合物および PTFE 以外のフッ素樹脂のばあい：「キャピラリーフローテスト」法

[0043]

[Effect of the invention] According to the technique of this invention, since it fabricates with injection molding, the fluororesin sintered compact of the complicated configuration with difficult molding can be sold at a cutting. Moreover, since there is no futility cutting off an excessive resin and a manufacturing process is also simplified in order not to apply a cutting process, the large cost cut of a product is possible.

[0044] According to this invention, since melting is carried out and injection molding is carried out at



the temperature below the melting point of a fluororesin, it is considered that fluororesins are one sort of fillers, and a low-temperature resolvability binder gives a fluidity and firmness. At this time, if a binder is a solid-state at a room temperature, a mold-release characteristic will also become good.

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[Translation done.]